THE PERCENT OF TITRATABLE AMINE
NEUTRALIZED WITH PHOSPHRIC ACID

FIG. 1

THE PERCENT OF TITRATABLE AMINE
NEUTRALIZED WITH PHOSPHORIC ACID

FIG. 2
ACID SALTS OF POLYSOBUTENYL ALKYLENE POLYAMINES AS FUEL DETERGENTS

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9 Claims

ABSTRACT OF THE DISCLOSURE

Mineral acid salts of hydrocarbyl substituted polynamines, which are substantially free of aromatic unsaturation and of from about 460 to 10,000 molecular weight, find use as detergents in fuels, particularly in combination with a small amount of oil.

BACKGROUND OF THE INVENTION

Field of the invention

Deposits resulting from polymeric materials in fuels remain a continuing problem in the smooth operation of internal combustion engines. Recently, a number of fuel detergent additives have been incorporated into fuels to reduce deposit formation. These additives help by maintaining various parts of the engine in clean condition and reduce incomplete combustion. Thus, the additives contribute to longer engine life, improved fuel performance and reduction in the production of smoke-producing exhaust products.

In co-pending application Ser. No. 647,611, filed on June 21, 1967 and now U.S. Pat. No. 3,438,757 hydrocarbyl polynamines are reported as detergents in fuels. It is found, however, that when the fuels are shaken with water, the separation of the fuel from the water and the clarity of the fuel phase are not as good as is desired. This phenomenon referred to as "water tolerance" varies, depending on the composition of the hydrocarbyl polynamine.

The problem of water tolerance can be acute with fuels which come in contact with water. In many storage tanks, the housekeeping is fairly poor and water collects at the bottom of the tank. When the fuel is introduced into the tank or withdrawn, significant agitation may occur. If the fuel and water do not separate quickly, significant amounts of water may be withdrawn with the fuel. Or, a cuff results, which means loss of fuel. If water is retained in the fuel phase, the fuel will appear hazy and could be unacceptable.

Also, by transferring by means of a centrifugal pump can result in "homogenization" of water and fuel, if a water phase is present in the holding tank. Rapid separation of the water from the fuel is essential, if the fuel is to be in condition for use.

Since fuel detergents are ordinarily good emulsifiers, the addition of detergents to fuels creates water tolerance problems. Solutions to the water tolerance problem have varied from modification of the detergent to the addition of a variety of demulsifiers.

Description of the prior art


SUMMARY OF THE INVENTION

Mineral acid salts of high molecular weight branched chain aliphatic hydrocarbon N-substituted alkylene polyamines are provided as detergents and dispersants having good water tolerance. These salts are particularly useful for extended detergent action in hydrocarbonaceous liquid fuels for internal combustion engines. The hydrocarbon substituted amine portion of the molecule has average molecular weights in the range of about 460 to 10,000, more usually in the range of about 600 to 5,000.

FIG. 1 is a graph of haze rating versus time for water tolerance determinations according to a modified version of ASTM D 1094-57, wherein polysobutyl tetaethylpentamine is neutralized to varying degrees with phosphoric acid.

FIG. 2 is a graph of the emulsion volume versus time for the same compositions employed for FIG. 1 and under the same test conditions.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The compositions which find use in this invention will, for the most part, have the following formula:

\[
\text{R}(-\text{N}(-\text{R'}\text{H})_{-\text{n}}\text{N}(-\text{H})\text{R}_2\text{H}_{-\text{n}}\text{H})\text{R}_1\text{H}_{-\text{n}}\text{H}+\text{\text{H}}_2\text{O}
\]

wherein \(R\) is alkyloxy of from 2 to 6 carbon atoms, more usually of from 2 to 3 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms. \(R'\) is an aliphatic hydrocarbon radical of from about 420 to 5,000 average molecular weight. \(a\) is an integer from 0 to 10; \(b\) is an integer from 0 to 1; \(c+2b\) is an integer from 1 to 10; \(c\) is an integer from 1 to 50, and \(n\) is an integer in the range of 0.1 to \(a+2b\); \(n\) is the number of titratable protons of the mineral acid \(Y\); and, \(Y\) is sulfuric acid or phosphoric acid.

The alkyloxy polynamine is titrated to determine the amount of titratable base. The method of titration will be described in the experimental section. From 10 up to about 50 percent, usually 15 to 60 percent, of the titratable base is neutralized with the mineral acid.

With the polybasic acids used, the acid will be titrated to determine the available acidity and the amine and acid combined in the proportion according to the titrimetric determination.

Preferred compositions will have the following formula:

\[
\text{R}(-\text{N}(-\text{R'}\text{H})_{-\text{n}}\text{N}(-\text{H})\text{R}_2\text{H}_{-\text{n}}\text{H})\text{R}_1\text{H}_{-\text{n}}\text{H}+\text{\text{H}}_2\text{O}
\]

wherein \(R\) is an oil soluble branched chain aliphatic hydrocarbon radical of from about 450 to 5,000 average molecular weight, usually polypropylene or polyisobutylene; \(R'\) is alkyloxy of from 2 to 3 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms; \(Y\) is phosphoric acid or sulfuric acid; \(a\) is an integer from 1 to 5; \(c+1\) is an integer from 1 to 5; \(c\) is in the range from 0.1 to \(a+1\); and, \(n\) is the number of titratable protons of the mineral acid \(Y\).

The compositions of this invention are readily prepared by combining in a suitable medium or neat, the acid and the amine. Cooling may be desirable or slow addition of the acid to the amine to avoid undue exothermicity.

The polynamaine compositions which find use in this invention are for the most part described by the following formula:

\[
\text{R}(-\text{N}(-\text{R'}\text{H})_{-\text{n}}\text{N}(-\text{H})\text{R}_2\text{H}_{-\text{n}}\text{H})\text{R}_1\text{H}_{-\text{n}}\text{H}+\text{\text{H}}_2\text{O}
\]

The above symbols are defined as follows:

\(\text{R}\) = alkyloxy of from 2 to 6 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms and preferably of from 2 to 3 carbon atoms.
R²—an aliphatic hydrocarbon radical, usually a branched chain aliphatic hydrocarbon radical of from about 400 to 5,000 average molecular weight, preferably of from 3,000 to 5,000 average molecular weight.

α—an integer of from 0 to 5

β—an integer of from 0 to 1

α+2β—an integer in the range of from 1 to 5

γ—an integer of from 1 to 4, for the average composition being in the range of about 1 to 3, on the average there being fewer R³ groups than nitrogen atoms.

The alkyne radical indicated as U² will have from 2 to 6 carbon atoms and more usually, from 2 to 3 carbon atoms, the nitrogen atoms connected by U² being separated by at least 2 carbon atoms. The alkyne group may be straight or branched chain and is preferably polyethylene of from 2 to 3 carbon atoms.

Illustrative alkylene groups are ethylene, 1,2-propylene, 2,3-dimethyl propylene-1,3, trimethylene, hexamethylene, 2-methyl-1,3-propylene, etc.

The alkylene polymers which are substituted with the hydrocarbon radical may be derived from such alkylene polymers as ethylene diamine, diethylene triamine, tetraethylene pentamine, nonaethylene decamine, 2-aminoethyl piperazine, 1,3-propylene diamine, 1,2-propylene diamine, tetramethylene diamine, etc.

In many instances a single compound will not be used as a reactant in the preparation of the compositions of this invention. That is, mixtures will be used in which one or two compounds will predominate and the average composition or molecular weight is indicated. For example, tetraethylene pentamine prepared by the polymerization of 1,2,3,4-azidine or reaction of dichloroethylene and ammonia will have both lower and higher members, e.g., triethylene tetramine and pentamethylene hexamine, but the composition will be mainly tetraethylene pentamine and the empirical formula of the total composition will closely approximate that of tetraethylene pentamine. Similarly, the molecular weight reported for the branched chain aliphatic hydrocarbon group is an average for a mixture which is sharply peaked when graphing the number average molecular weight distribution. Also, when the nitrogens of the 3,000,000 average molecular weight are not equivalent, substitution on different nitrogens will afford different compounds.

As is evident from the above formulae, the alkylene polymers may have only one hydrocarbon substituent or may be polysubstituted with hydrocarbon radicals. The monosubstituted alkylene polymer compositions will have the following formula:

\[ \left[ -\text{N} \left(-\text{CRH} \right) _{n} \text{N} \left(-\text{CRH} \right) _{m} \text{S} \left(-\text{N} \text{CH}_{2} \text{CH}_{3} \text{N} \right) _{s} \right] \text{R}_{3 \text{H}} \text{R}_{4} \text{R}_{5} \text{R}_{6} \]

The above symbols are defined as follows:

α—an integer of from 0 to 5, preferably from 0 to 4

β—an integer of from 0 to 1, preferably 0 when α is greater than 0

α+2β—an integer of from 1 to 5

γ—an integer of from 2 to 3

R²—a branched aliphatic hydrocarbon radical derived from polymerizing olefins of from 2 to 6 carbon atoms, preferably from 2 to 4 carbon atoms, and particularly preferred are propylene and isobutylene and having an average molecular weight in the range of 400 to 3,000, preferably 400 to 2,500.

Illustrative compounds within the above formula are as follows: N-polyisobutylene ethylene diamine, N-polypropylene ethylene diamine, N-polyisobutylene ethylene diamine, N-ethylenediamine. When the alkyne is ethylene diamine, N-(alternating copolymer of ethylene and isobutylene) ethylene diamine (alternating copolymers of ethylene and isobutylene may be achieved by the cationic polymerization of 4-methylpentene-1), N-polypropylene 2-aminoethylpiperazine, N- polyisobutylene 2-aminoethylpiperazine, N-polypropylene diethylene triamine, N-polyisobutylene diethylene triamine, N-polyisobutylene triethylene diamine, N-polypropylene triethylene diamine, N-polyisobutylene triethylene diamine, N-(alternating copolymer of ethylene and isobutylene) triethylene diamine, N-polypropylene tetraethylene pentamine, N-polypropylene tetrathylenepentamine, N-polyisobutylene tetraethylene pentamine, N-polypropylene hexamethylene diamine, etc.

The polyhydrocarbon radical substituted alkylene polyamine compositions have the following formula:

\[ \left[ -\text{N} \left(-\text{CRH} \right) _{n} \text{N} \left(-\text{CRH} \right) _{m} \text{S} \left(-\text{N} \text{CH}_{2} \text{CH}_{3} \text{N} \right) _{s} \right] \text{R}_{3 \text{H}} \text{R}_{4} \text{R}_{5} \text{R}_{6} \text{R}_{7} \text{R}_{8} \]

The above symbols are defined as follows:

α—an integer of from 0 to 5, preferably an integer of from 1 to 4

β—an integer of from 0 to 1, preferably 0 when α is greater than 0

α+2β—an integer of from 1 to 5

γ—an integer in the range of 1 to 3, on the average there being fewer R³ groups than nitrogen atoms

δ—an integer of from 2 to 3

R²—a branched chain aliphatic hydrocarbon radical either free of or having aliphatic unsaturation, e.g., olefinic and of from 400 to 3,000 average molecular weight, preferably of from 400 to about 2,500 average molecular weight.

(As indicated by the above formula, the number of hydrocarbon substituents need not be a whole number when averaged over a total composition; generally, a mixture will be obtained containing mono-, di- and tri- or higher substituted molecules averaging out to a fractional or whole number.)

Illustrative compounds coming within the above formula are as follows: N,N'-di(polypropylenyl) diethylene triamine, N,N'-di(polyisobutylene) diethylene diamine, N,N'-di(polyisobutylene) triethylene tetramine, N,N'-di(polypropylene) tetraethylene pentamine, N,N'-di(polyisobutylene) tetraethylene pentamine, N,N'-di(polyisobutylene) 2-aminoethylpiperazine, N,N'-di(polyisobutylene) triethylene tetramine, N,N'-di(polyisobutylene) di(triethylene) triamine, etc.

The preferred compositions are those having the straight chain alkylene polyamines, particularly ethylene diamine and polyethylene polyamines. These compositions have the following formula:

\[ \left[ -\text{N} \left(-\text{CRH} \right) _{n} \text{N} \left(-\text{CRH} \right) _{m} \text{S} \left(-\text{N} \text{CH}_{2} \text{CH}_{3} \text{N} \right) _{s} \right] \text{R}_{3 \text{H}} \text{R}_{4} \text{R}_{5} \text{R}_{6} \text{R}_{7} \text{R}_{8} \]

The above symbols are defined as follows:

α—an integer of from 1 to 5, preferably of from 1 to 4

β—an integer in the range of 1 to 3, on the average over the entire composition being in the range of from 1 to 2, per molecule there being fewer R³ groups than nitrogen atoms

R²—a branched chain aliphatic hydrocarbon radical of from 400 to 3,000 average molecular weight, preferably of from 400 to 2,500 average molecular weight, and, particularly preferred, either polypropylene or polyisobutylene.

The preparation of the polyamines is usually carried out by combining a halogenated aliphatic hydrocarbon of the appropriate molecular weight with the desired amine. An extensive discussion of the method of preparation is found in copending application Ser. No. 647,611, filed on June 21, 1967, and now U.S. 3,438,757.

The detergent will generally be employed in a hydrocarbon base liquid fuel. The detergent additive may be formulated as a concentrate, using a suitable hydrocarbon alcohol solvent boiling in the range of about 150° to 400° F. Preferably, an aromatic hydrocarbon solvent is
used, such as benzene, toluene, xylene or higher boiling aromatics or aromatic thinners. Aliphatic alcohols of about 3 to 8 carbon atoms, such as isopropanol, isobutyl alcohol, and butyl alcohol, and also lead scavengers such as aryl halides, e.g., dichlorobenzene or alkyl halides, e.g., ethylene dibromide.

A nonvolatile lubricating mineral oil, e.g., petroleum spray oil, particularly a refined naphthenic lubricating oil having a viscosity at 100°F of 1,000 to 2,000 SUS is a suitable additive for the gasoline compositions used with the detergents of this invention and its use is preferred. These oils are believed to act as a carrier for the detergent and assist in moving and preventing deposits. They are employed in amounts from about 0.05 to 0.5 percent by volume, based on the final gasoline composition.

EXAMPLES

The following examples are offered by way of illustration and not by way of limitation.

Example A

Polyisobutenyl chloride (10,170 lbs.) (polyisobutenyl ~1,000 average molecular weight; percent Cl ~6.2) was charged to a reaction vessel and warmed to 250°F. To the reaction vessel was added 4,360 lbs. of tetraethylene pentamine (a commercial mixture of polyalkylene polyamines having the indicated average composition) and 1,510 lbs. of n-butanol.

The reaction mixture was purged with nitrogen and the temperature raised to 300°F and maintained for 8 hrs. with agitation. At the end of this time, the mixture was cooled to 200°F and 1,000 gal. of an aromatic solvent (boiling range 316–327°F) added. While stirring and maintaining the temperature between 170–200°F, 108 gal. of isopropyl alcohol and 520 gal. of hot water was added and the mixture stirred for 7 hrs. The aqueous layer was withdrawn and the aqueous isopropyl alcohol washed repeated 3 times. Volatile material was then distilled, raising the temperature to a final temperature of 280°F.

The product was then mixed with 100 lbs. of flake caustic, followed by the addition of distomaceous earth. After agitating the mixture, the product was filtered. The filtrate was diluted with the aromatic solvent described above to provide a solution analyzing to 3.13% N₂ ~51 weight percent active.

Example I

Into a reaction vessel was combined one gram of phosphoric acid (86 weight percent) and 13 g. of xylene. To the acidic solution was slowly added 10 g. of a composition prepared as described in Example A (50 weight percent active) with agitation. The final product had active material in a concentration of 25 weight percent and the amine was 55.5 percent neutralized.

Example II

Following the procedure of Example I, 0.65 g. of sulfuric acid (96 weight percent) and 11.83 g. of xylene were combined. To the acidic solution was slowly added with agitation 10 g. of a composition prepared as described in Example A. The final solution had 5 weight percent active material and the amine was 90 percent neutralized. Titrations were carried out as follows. The amine is obtained as a 50 weight percent solution of active material (determined by nitrogen analysis, assuming one hydrocarbon group per polyamine molecule) in a C₉ aromatic solvent. Approximately 0.5 g. is dissolved in a solution having 20 volumes of benzene, 75 volumes of isopropyl alcohol and 5 volumes of distilled water. The solution is potentiometrically titrated with approximately 0.1 normal HCl, graphing the percentage the titration. The midpoint of the curve (pH ~5.3) determines the amount of titratable nitrogen.

The acid is titrated in aqueous media to a pH of 7. For phosphoric acid, only the first proton is titrated.

To demonstrate the effectiveness of the amine salts of this invention as fuel detergent and base fuel having a boiling range of 102 to 414°F; 58 percent paraffins, 22 percent aromatics, and 20 percent olefins (by volume) and a vapor pressure (Reid) of 7.4 was employed. The additive was added at a concentration of 250 p.p.m.

The test was carried out with a single cylinder CFR engine equipped with throttle. The operating conditions for the test are: jacket temperature, 212°F; oil temperature, 150–180°F; intake air temperature, 95°F; ignition timing, 15° BTC; intake manifold vacuum, 15 in. Hg; fuel/air ratio; 0.07; speed, 1,800 r.p.m. The duration of the test is 12 hrs.

The intake valve is weighed at the end of the test, cleaned and tared. The intake port is washed with hexane, then cleaned with a receiver, and the deposits removed mechanically with the aid of chloroform. The chloroform is evaporated at about 250°F. and the deposits weighed.

The following table indicates the results:

<table>
<thead>
<tr>
<th>Port deposits</th>
<th>Valve deposits</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg.</td>
<td>mg.</td>
</tr>
<tr>
<td>Base fuel</td>
<td>129(7)</td>
</tr>
<tr>
<td>Plus Ex. T.</td>
<td>7.9(0)</td>
</tr>
</tbody>
</table>

The values reported are the average from the number of determinations indicated in parenthesis.

To demonstrate the excellent water tolerance of the salt mixtures employed in this invention, the test procedure of ASTM D 1049–57 was employed. The following table indicates the results obtained after 10 minutes, using distilled water. The haze rating is a rating based on a rating of 1 to 5; the cylinder is observed against a flat vertical plate of diffused white light. Horizontal black strips are affixed to the surface of the plate. The graduated cylinder is placed in front of the plate and the haze rating determined by the degree of diffuseness of these black strips. A sharp appearance is rated as 1; an almost totally obscured strip is rated as 5.

<table>
<thead>
<tr>
<th>Additive</th>
<th>350 p.p.m.</th>
<th>Haze</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex. 1</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Ex. 2</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

1 Polyisobutenyl tetraethylenepentamine ~13 mol ratio of hydrocarbons to alkylene polyamines; tetraethylenepentamine is a mixture of alkylenepolyamines having the indicated composition: sodium polyisobutenyl has an average molecular weight of about 1,000.

2 The procedure and reagents of Example II were employed, but the degree of neutralization was only 95%.

To further demonstrate the excellent water tolerance of the invention, FIGS. 1 and 2 provide a comparison of polyisobutenyl polyamine (the polyamine having an average composition equal to tetraethylenepentamine, there being approximately 1 polyisobutenylene of about 1,000 molecular weight) per alkylene polyamine being neutralized with phosphoric acid to various degrees.

The significant improvement in water tolerance is evidenced by the increase in rate at which the water and fuel layer separate and the black strips develop.

Both rapid separation and reduction in haze are important in evaluating water tolerance. For, even in the situation where the water separates quickly, if a small residual amount of water remains dispersed in the fuel
giving it a hazy appearance, the fuel will be unacceptable. Frequently, haze and water separation do not directly correlate. Therefore, it is important that with the exemplary phosphate salt, great improvement in both the haze rating and separation is achieved, and a rapid reduction in haze and a quick separation between the fuel and water layers is obtained.

It is evident from the above results that while the detergent effectiveness in fuels is substantially retained with the mixture of salt and amine, when the phosphate or sulfate anions are employed, enhanced water tolerance is achieved over the parent amine. Thus, not only is excellent detergency achieved, but the fuel is also found to have excellent water tolerance. This is particularly surprising when one is using a highly detergent material, which generally causes emulsions; and, by going to a more polar situation, one achieves enhanced water tolerance.

I claim:

1. A liquid hydrocarbon fuel composition having from 50 p.p.m. to 1000 p.p.m. of a detergent additive of the formula:

\[ \text{(x/1)}Y\{-(\text{N}-U-N_4\}(-UN\{N-3b)R_b\text{R}_{4-x/b}\} \]

wherein U is alkylene of from 2 to 6 carbon atoms, usually of from 2 to 3 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms; R is a branched chain aliphatic hydrocarbon radical of from about 420 to 5000 average molecular weight; a is an integer of from 0 to 10; b is an integer of from 0 to 1; a+2b is an integer of from 1 to 10; c is an integer of from 1 to 5 and averages in the range of 1 to 4 over the entire composition and is less than the number of amine nitrogens in the molecule; x is in the range from 0.1 to a+2b; and, n is the number of acidic protons of the mineral acid Y which can be titrated below pH 7; and, Y is sulfuric acid or phosphoric acid.

2. A fuel composition according to claim 1, wherein said detergent additive is of the formula:

\[ \text{(x/1)}Y\{-(\text{N}-U-N_4\}(-UN\{N-3b)R_b\text{R}_{4-x/b}\} \]

wherein R is an oil soluble branched chain aliphatic hydrocarbon radical of from 450 to 5000 average molecular weight; U is alkylene of from 2 to 3 carbon atoms; Y is phosphoric acid; a is an integer of from 1 to 5; c is an integer of from 1 to 5 and equal to or less than a; x is in the range from 0.1 to a; and, n is the number of protons titratable below pH 7 of the mineral acid Y.

3. A fuel composition according to claim 2, wherein x does not exceed 60 percent of the titratable amine nitrogen.

4. A fuel composition according to claim 2, wherein R is polyisobutyl.

5. A composition of matter having the formula:

\[ \text{(x/1)}Y\{-(\text{N}-U-N_4\}(-UN\{N-3b)R_b\text{R}_{4-x/b}\} \]

wherein U is alkylene of from 2 to 6 carbon atoms, usually of from 2 to 3 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms; R is an aliphatic hydrocarbon radical of from about 420 to 5000 average molecular weight; a is an integer of from 0 to 10; b is an integer of from 0 to 1; a+2b is an integer of from 1 to 10; c is an integer of from 1 to 5 and averages in the range of 1 to 4 over the entire composition and is less than the number of amine nitrogens in the molecule; x is in the range from 0.1 to a+2b; and, n is the number of acidic protons of the mineral acid Y which can be titrated below pH 7; and, Y is sulfuric acid or phosphoric acid.

6. A composition of matter having the formula:

\[ \text{(x/1)}Y\{-(\text{N}-U-N_4\}(-UN\{N-3b)R_b\text{R}_{4-x/b}\} \]

wherein R is an oil soluble branched chain aliphatic hydrocarbon radical of from 450 to 5000 average molecular weight; U is alkylene of from 2 to 3 carbon atoms; Y is phosphoric acid; a is an integer of from 1 to 5; c is an integer of from 1 to 5 and equal to or less than a; x is in the range from 0.1 to a; and, n is the number of protons titratable below pH 7 of the mineral acid Y.

7. A composition of matter according to claim 6, wherein R is polyisobutyl.

8. A liquid hydrocarbon fuel concentrate composition having from 10 to 70 weight percent of a composition according to claim 5 in a suitable solvent boiling in the range of about 150 to 400°F.

9. A liquid hydrocarbon fuel composition having from 50 p.p.m. to 1000 p.p.m. of a polyisobutyl tetrachloroethylene pentamine, wherein said polyisobutyl group is of from about 400 to 2500 average molecular weight, wherein said polyisobutyl tetrachloroethylene pentamine is neutralized to from 15 to 60 percent with phosphoric acid.

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